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EFFECTS OF THERMAL AND ENVIRONMENTAL EXPOSURE ON THE MECHANICAL PROPERTIES OF GRAPHITE/POLYIMIDE COMPOSITES

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16. Abstract
Composites were exposed in circulating and static air environments up to 589 K (600° F) for a maximum of 1000 hours. Composites of HT-S, HM-S, Thornel 50S, and Fortafil 5-Y fiber and a new addition type polyimide resin were laminated in a matched-die mold. Flexural strength, flexural modulus, and interlaminar shear strengths were determined at 297, 533, and 598 K (75°, 500°, and 600° F) after various durations of exposure. Composite and fiber weight loss characteristics were determined by isothermal gravimetric analysis in air. Properties of composites exposed and tested at the environment temperatures are compared with those determined under short-term exposure. A new short beam interlaminar shear fixture is described. Environmental effects of long-term (up to 1 year) ambient temperature exposure on the elevated temperature mechanical properties of graphite/polyimide composites are presented.

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SUMMARY

Composites of HT-S, HM-S, Thornel 50S, and Fortafil 5-Y fiber and a new addition type polyimide resin were exposed in circulating and static air environments up to 600° F for a maximum of 1000 hours. Fabrication of fiber and resin resulted in composites of low-void content (less than 3.0 percent). Flexural strength, flexural modulus, and shear properties were generally retained up to 1000 hours of exposure at 533 K (500° F). However, at 589 K (600° F) the properties degraded significantly after 300 to 400 hours of exposure. HT-S composites had a greater percent reduction of elevated temperature properties compared to HM-S, Thornel 50S, or Fortafil 5-Y composites. HT-S fiber also showed a higher weight loss than did the HM-S, Thornel 50S, or Fortafil 5-Y fibers after exposure at 589 K (600° F) in air for 1000 hours. Comparisons between high- and low-void-content composites showed that high-void content markedly accelerated the degradation of composite properties at both 533 and 589 K (500° and 600° F). Long-term exposure of graphite/polyimide composites to ambient temperature and humidity conditions had no significant effect on the elevated temperature flexural strength.

INTRODUCTION

Difficulties associated with processing high-temperature-resistant resins have limited their use as matrix resins in advanced-fiber/resin composites. Recently under NASA sponsorship, TRW Incorporated developed a novel class of processable high-temperature resins known as A-type polyimides (ref. 1). A-type polyimides cure without the release of volatile byproducts enabling high-quality void-free composites to be fabricated.

The purpose of the present investigation was to determine certain mechanical properties for several graphite/resin composites with an A-type polyimide matrix common to all specimens. In addition, it was proposed to investigate the effects produced by short- and long-term exposure at elevated temperatures.

The work reported herein was performed on composites fabricated using graphite fibers and a more recently developed A-type polyimide known as P10P (ref. 2). Graphite fibers used in this study included HT-S, HM-S, Thornel 50S, and Fortafil 5-Y. Flexural and interlaminar shear properties are reported for unidirectional fiber composites exposed and tested in air at 297, 533, and 589 K (75°, 500°, and 600° F).

MATERIALS AND FABRICATION

The graphite fibers used in this investigation are listed in table I. The properties listed are typical values taken from the manufacturers' literature. All fibers are continuous-filament yarns or tows except Fortafil 5-Y which is a continuous staple fiber yarn. The fibers were surface treated by the manufacturers to improve interlaminar shear. The nature of the surface treatments is proprietary. In addition to being surface treated, the Thornel 50S was sized with P10P by the manufacturer.

TABLE I. - TYPICAL PROPERTIES OF GRAPHITE FIBERS[a]

Fiber	Specific gravity	Tensile strength[b]		Elastic modulus[b]	
		N/cm^2	psi	N/cm^2	psi
HT-S[c]	1.74	207×10^3 to 276×10^3	300×10^3 to 400×10^3	24.2×10^6 to 29.0×10^6	35×10^6 to 42×10^6
HM-S[c]	1.90	173×10^3 to 224×10^3	250×10^3 to 325×10^3	34.5×10^6 to 41.4×10^6	50×10^6 to 60×10^6
Thornel 50S[d]	1.68	138×10^3	200×10^3	34.5×10^6	50×10^6
Fortafil 5-Y[e]	1.90	173	250×10^3	34.5×10^6	50×10^6

[a]Impregnated with P10P resin (40 percent solids in DMF) TRW Systems Group.
[b]Typical properties reported by manufacturer.
[c]Hercules Corporation.
[d]Union Carbide Corporation.
[e]Great Lakes Carbon Corporation.

All fibers for isothermal degradation studies were impregnated with the P10P resin during drum winding. After winding, the solvent content was reduced from 40 to 30 percent by heating at 322 K (120° F) for 30 minutes to produce a tacky, handleable prepreg. The prepreg was cut to mold size (7.62 by 25.4 cm or 3 by 10 in.) with the longitudinal axis of the fibers in the 25.4-centimeter (10 in.) direction. Individual plies were placed in an air circulating oven at 394 K (250° F) for 10 minutes to further reduce the solvent content to about 15 percent. The necessary number of plies required for a final laminate thickness of about 1.78 millimeter (0.07 in.) were heated (imidized) at 477 K (400° F) for

2 hours. The resultant preform was placed between aluminum foil as a parting material. The final cure consisted of molding the preform in a matched-die mold in a heated press at 589 K (600° F) and 345 newtons per square centimeter (500 psi) for 30 minutes. A 20-second dwell time was used. The mold pressure was reduced to 17.3 newtons per square centimeter (25 psi) and the platens were cooled to ambient temperature before removal of the laminate. No post curing was performed in this investigation. The fiber content of the fabricated laminates ranged from 56 to 61 percent. The method used to determine the fiber content is described in reference 3. Average void contents of less than 3.0 percent were determined. A photomicrograph of an essentially void free Thornel 50S/P10P laminate is shown in figure 1. The void content was determined by relating the calculated and measured specific gravities.

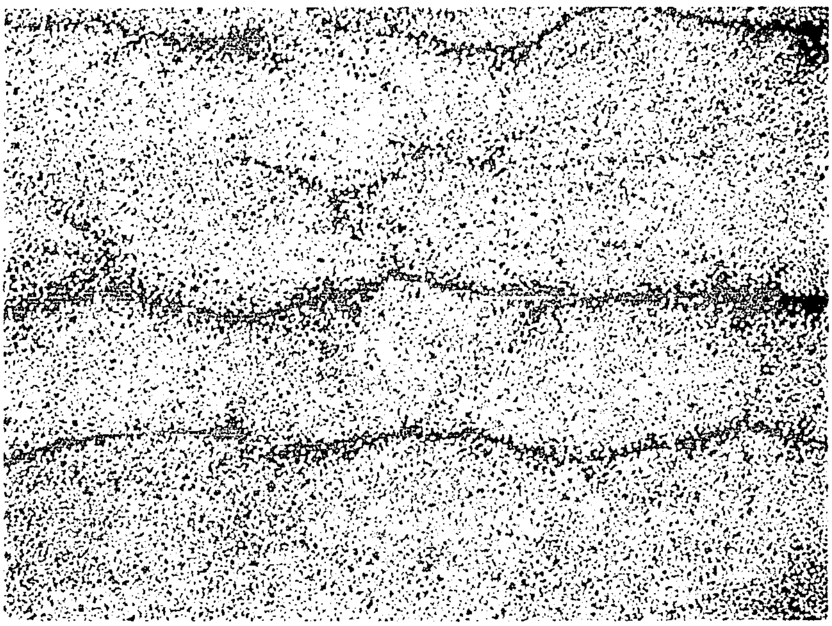

Figure 1. - Photomicrograph of P10P/Thornel 50S composite showing low void content. X100.

APPARATUS AND PROCEDURE

Isothermal Environment

Forced convection air ovens were used for the long-term isothermal environment at 533 and 589 K (500° and 600° F) for most of the composite material. Makeup air was metered into the ovens at a rate of 100 cubic centimeters per minute at atmospheric pressure. The ovens were vented to the laboratory exhaust system. A static air chamber was provided for exposure of material at 589 K (600° F). Test coupons 12.7 millimeter (1/2 in.) wide by 25.4 centimeter (10 in.) long, were given various exposure times up to 1000 hours. At predetermined time intervals, the coupons were removed for weight loss determinations and cut to specimen size for flexural and interlaminar shear tests. Bare graphite fibers were also exposed to 589 K (600° F) in the forced convection air oven for 1000 hours to determine weight loss.

Flexural Tests

The flexural tests conformed essentially to the ASTM standard method D790-66. Tests were made on a three-point loading fixture with a fixed span of 5.08 centimeter (2.0 in.) to determine flexural strength and modulus. The specimens were 12.7 millimeter (1/2 in.) wide by approximately 7.6 centimeter (3 in.) long and had a nominal thickness of 1.78 millimeters (0.07 in.). The variation in specimen thickness resulted in span to thickness ratios ranging from 27 to 32. The rate of center loading was 1.27 millimeter (0.05 in.) per minute. The elevated temperature tests were performed in an environmental heating chamber. The temperature was controlled by a thermocouple probe located in close proximity to the test specimen. In the elevated temperature materials characterization tests, the specimens were loaded 15 minutes after the temperature had stabilized at the appropriate test temperature.

Interlaminar Shear Tests

Short-beam interlaminar shear tests were performed in the shear fixture shown in figure 2. This new concept in a shear fixture was developed to provide an easily-adjustable, infinitely variable span. The fixture consists of two movable end supports that are laterally guided in a fixed support. The supports move outward and inward with respect to each other to accommodate short-beam shear specimens of various lengths. Variable spans are made possible by left and right hand screw threads in the span adjustment screws. The midspan load is provided by a yoke and pin arrangement. The lower projections on the movable end supports retain the specimen while positioning the yoke and inserting the loading pin.

The shear fixture has many unique testing features. For example, by limiting the depth of the load support slots, it is possible to apply load at the immediate ends of the specimen. The fixture also permits interlaminar shear tests to be conducted at a constant span to thickness ratio regardless of specimen thickness. In practice, it is very difficult to mold laminates having identical thicknesses. However, with this fixture the

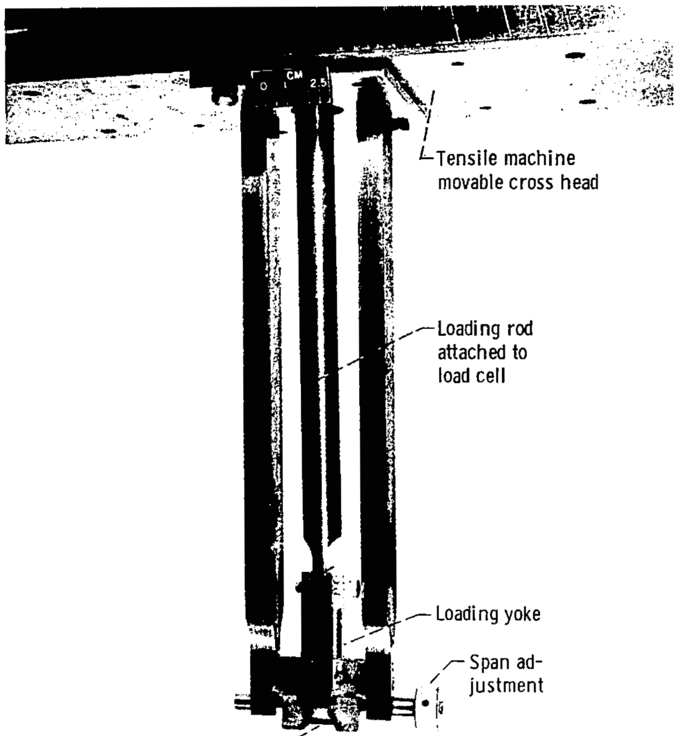

Figure 2. - Variable-span interlaminar shear fixture with loading yoke raised.

length of the specimen can be adjusted to provide a constant span to thickness ratio. In this investigation the distance between supports of the 6.35-millimeter (0.25-in.) wide specimens was adjusted to establish a 5:1 span to thickness ratio. The shear test environments were the same as for the flexural tests.

DISCUSSION AND RESULTS

The short and long term isothermal exposures at 533 or 589 K (500° or 600° F) were made for HT-S, HM-S, Thornel 50S, and Fortafil 5-Y fibers in a P10P resin matrix. The variations of flexural strength, flexural modulus, interlaminar shear strength, and weight loss as functions of time and elevated temperature are shown in figures 3 to 6. Also shown in the figures are the 297 K (75° F) mechanical properties. The data are an average of 3 or more tests at a given condition.

On short term exposure (1/4 hr) at 533 or 589 K (500° or 600° F), the composites containing high-modulus graphite materials HM-S, Thornel 50S, and Fortafil 5-Y (figs. 4 to 6) retain approximately 90 percent of their room-temperature flexural strength.

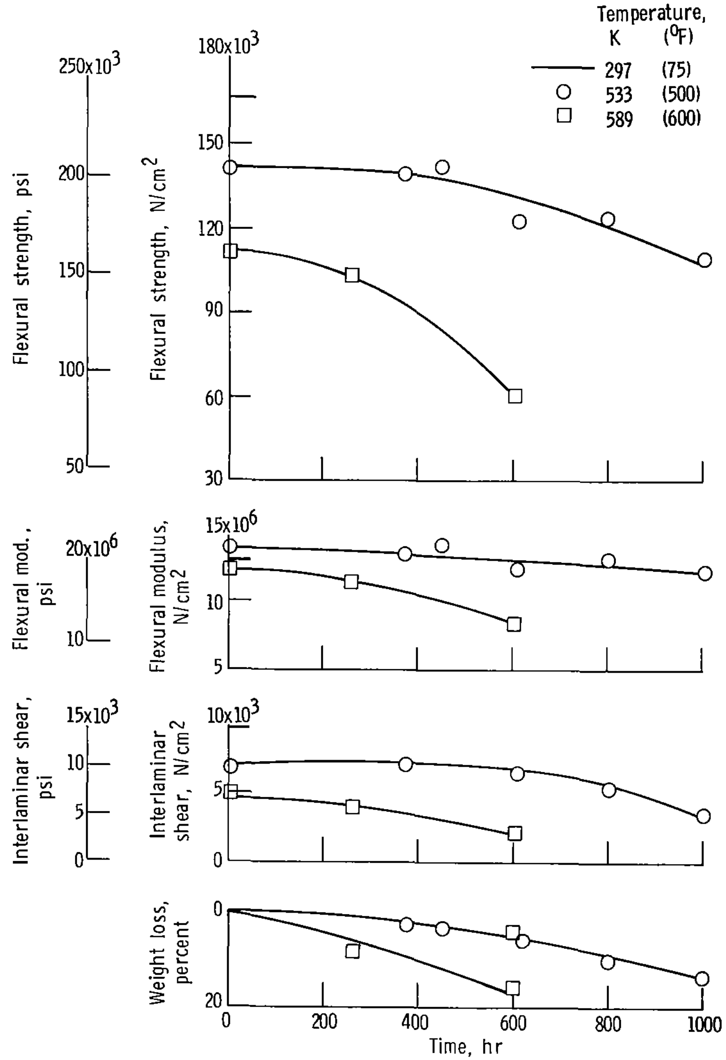

Figure 3. - Properties of HT-S/P10P composites as function of time at temperature.

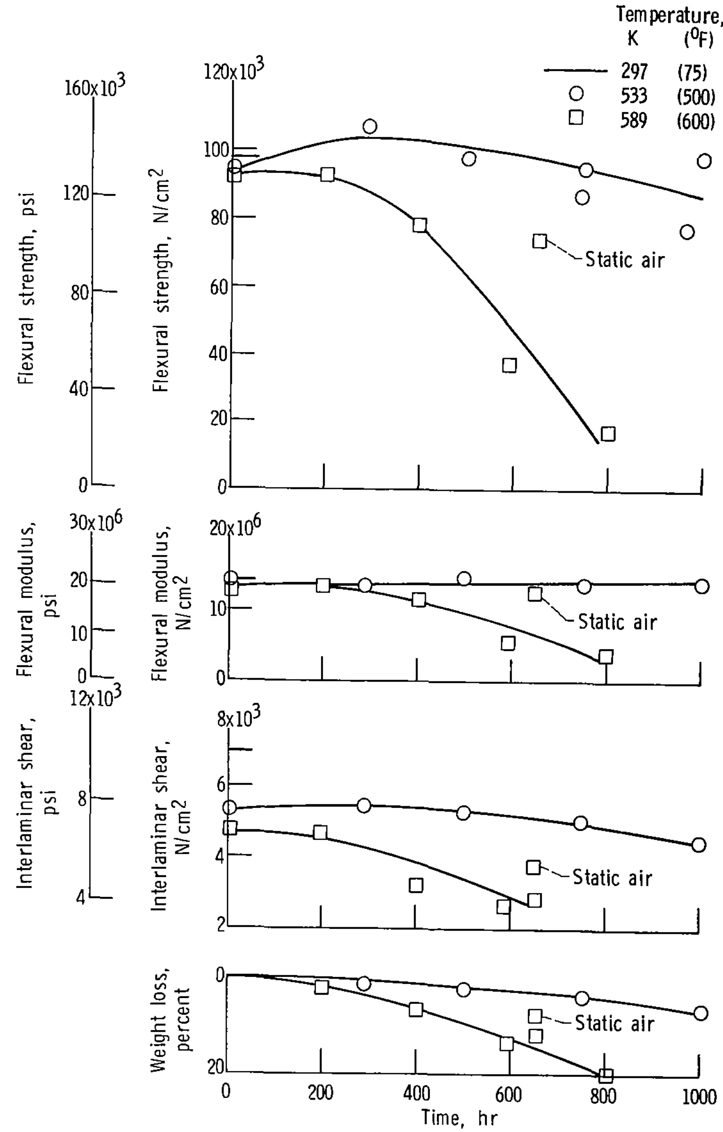

Figure 4. - Properties of HM-S/P10P composites as function of time at temperature.

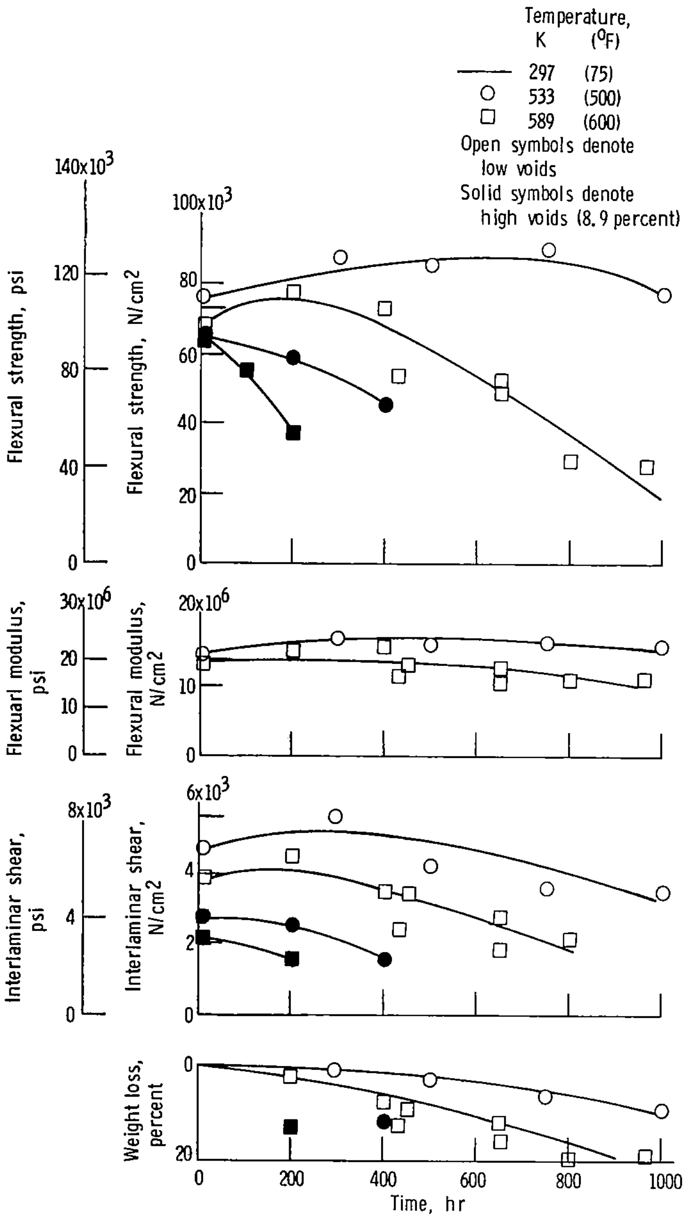

Figure 5. - Properties of T505/P10P composites as function of time at temperature.

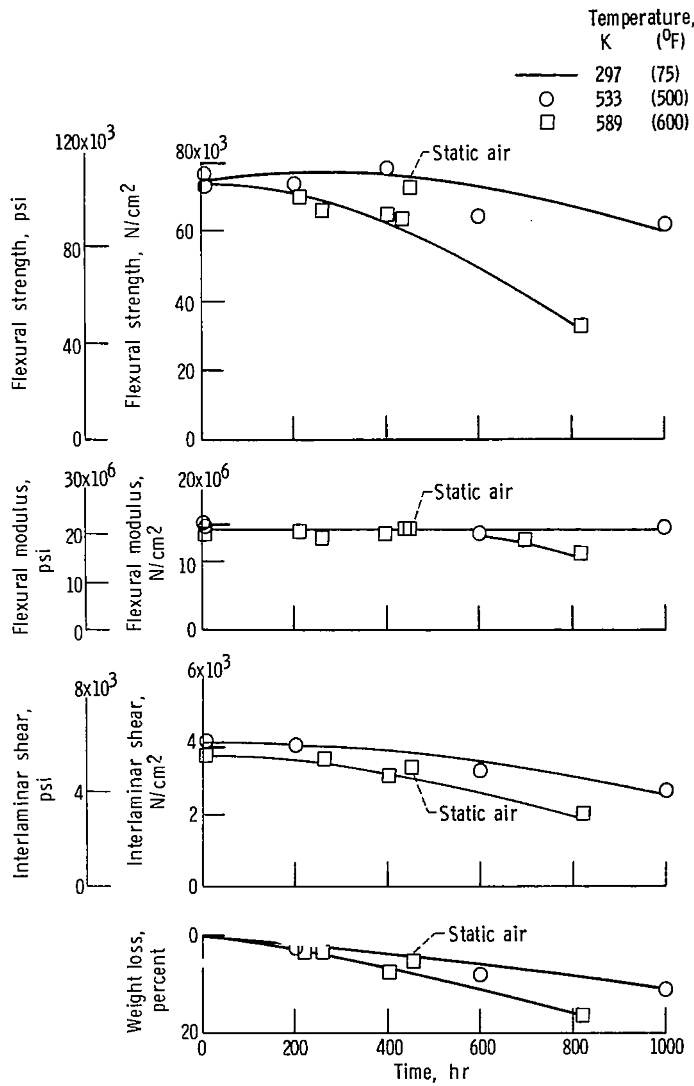

Figure 6. - Properties of 5-Y/P10P composites as function of time at temperature.

However, the flexural strength of the composites containing high-strength graphite HT-S shows a marked reduction at elevated temperature compared with 297 K (75° F) (fig. 3). At 589 K (600° F), the strength is reduced to 34 percent compared with that at 297 K (75° F). A similar type of behavior was noted for high-strength graphite fiber/P13N composites in reference 4.

On long term exposure at 533 K (500° F) the flexural strengths of the high-modulus fiber composites (HM-S, Thornel 50S, and Fortafil 5-Y) had good retention for the 1000-hour test. In fact, an increase in flexural strength after exposure for several hundred hours is observed. After 1000 hours the flexural strengths are essentially the same as the initial elevated temperature strengths. However, at 533 K (500° F) and after 1000 hours of exposure, the flexural strength of the high strength fiber composites (HT-S) showed a decrease of about 22 percent. At 589 K (600° F) and after 200 hours, all composites exhibited a pronounced increase in the rate of property degradation. For most composites the exposure at 589 K (600° F) was terminated at 600 hours because of fiber fragmentation and general loss of the structural integrity. The flexural strength results for the four composite materials are summarized in figure 7. Although no post curing was performed before exposure, the evidence of improved properties after exposure at 533 K (500° F) suggests that a post curing mechanism is operative.

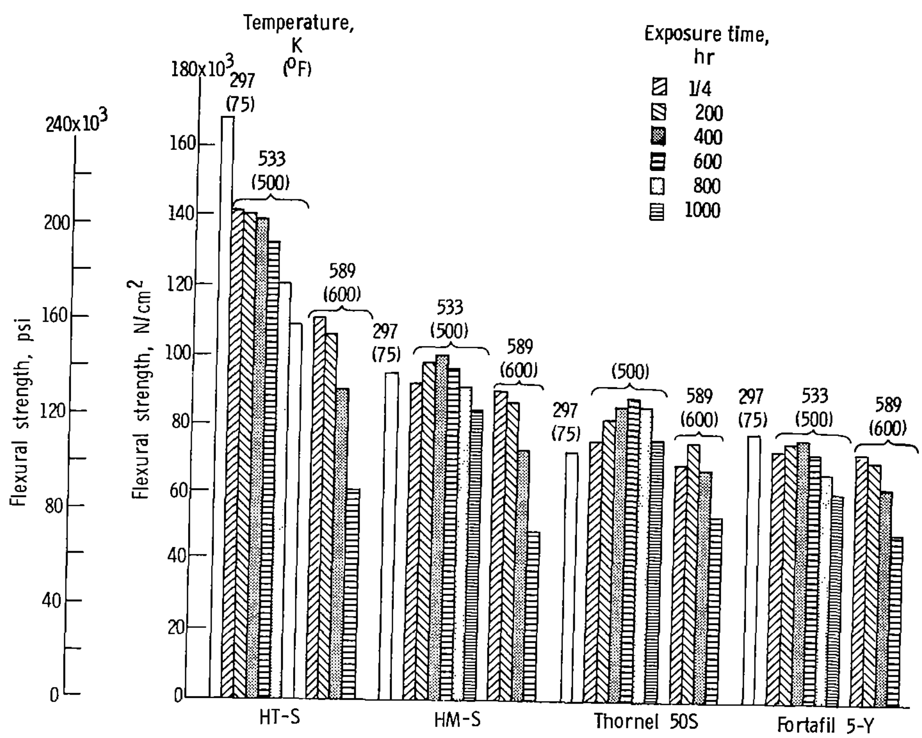

Figure 7. - Comparison of flexural strengths of various graphite/P10P composites at room temperature.

In the flexural tests, the mode of failure varied. The specimens failed either in shear, tension, or compression. Data from flexural specimens failing in shear were not included in the results because the fracture load for a shear failure is lower than that for a tensile or compressive failure. At room temperature the failure mode was tensile failure of the outer fibers or complete fracture of the specimen. After short-term exposure to 533 K (500° F), the failures were predominately tensile; however, at 589 K (600° F) the failures were predominantly compressive. Long-term exposure to 533 or 589 K (500° or 600° F) resulted in compressive failures. The sporadic shear failures occurred usually at elevated temperatures.

Unexpectedly, the flexural moduli of the high modulus fiber composites were not noticeably larger than those of the high strength fiber composites. On the basis of the fiber tensile moduli and the rule of mixtures, the moduli of the high modulus fiber composites would have been 35 percent higher. It is conceivable that the moduli did not translate because of possible variations in the shear modulus and fiber physical properties. Slight deviations of the fibers from the undirectional orientation and possible imperfections in the fiber/resin interface (ref. 5) could also have been contributing factors for the lower flexural moduli of the higher modulus fiber composites.

The degrading effect of elevated temperature is more pronounced on the interlaminar shear strength than on the flexural strength. At short-term exposure to temperature, the high modulus fiber composites had shear values 15 to 30 percent lower at 533 and 589 K (500° and 600° F) as compared with 30- to 50-percent reductions for the high strength fiber composites. These comparisons are shown in figure 8. Extended exposure to elevated temperature resulted in a general reduction of interlaminar shear strength.

It should be noted that certain experimental and environmental variables, in addition to elevated temperature, can markedly affect the properties of resin matrix composites. Reference 2 discussed the need to consider the effect of sample surface-area-to-volume ratio when testing composites exposed to elevated temperatures. In reference 6 it was found that increased environmental pressure at 589 K (600° F) increased the composite weight loss. It is possible that increased airflow also would accelerate the thermo-oxidative degradation of the resin. Figures 4 and 6 show limited results comparing properties of composites after exposure at 589 K (600° F) in static air to those in circulating air. It can be seen that the static air environment is significantly less degrading on all the measured properties. These elevated-temperature results indicate that the application environment can have an important influence on the performance of the material.

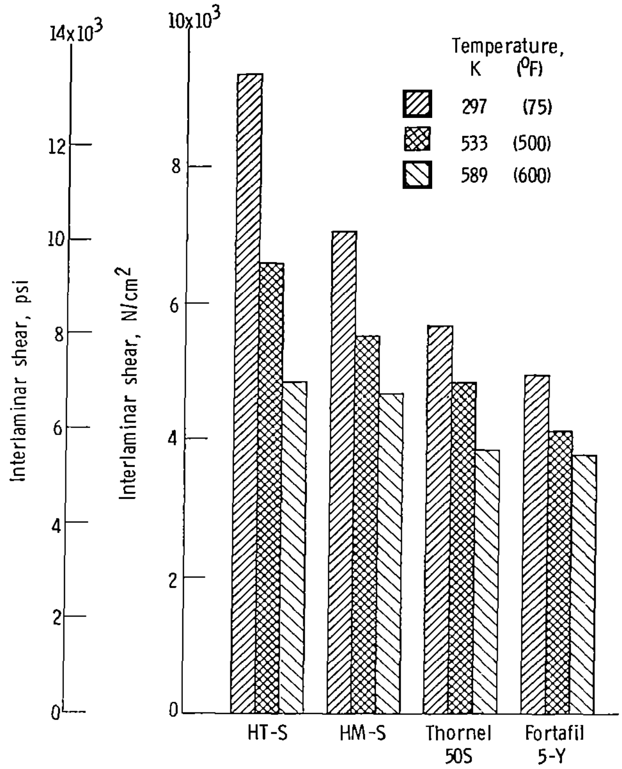

Figure 8. - Interlaminar shear strength of graphite/P10P composites after short term exposure. Span-to-thickness ratio, 5:1.

Void Effects

Voids have adverse effects on composite properties (ref. 6). As mentioned in the materials section, the P10P resin produced composites with low void content. Because of an inadvertent deviation from the standard laminating procedure, a Thornel 50S/P10P composite having a high void content (8.9 percent) was molded. Figure 5 shows that the high void content not only accelerates degradation of properties at elevated temperature exposure but also overshadows the effect of temperature. As shown in figure 5 the flexural strength retention of the high-void composite at 533 K (500° F) is inferior to the flexural strength retention of the low-void composite at 589 K (600° F). The high-void content even more adversely affects the interlaminar shear strength. At elevated temperature the shear properties for short-term exposure are approximately 50 percent lower. As expected, the rate of composite weight loss for the higher void composites exceeds the weight loss rate for low void composites.

The higher rates of property degradation and weight loss displayed by the higher void composites can be primarily attributed to increased thermo-oxidative degradation of the resin as a result of increased surface area-to-volume ratio. These results emphasize the need to minimize or eliminate entirely voids in composites intended for use at elevated temperatures.

Influence of Type of Fiber on Properties

The observed high-percentage reduction of elevated-temperature properties of the high-strength graphite composite is not readily explained. The high-strength fiber appears to undergo accelerated degradation at elevated temperature. Exposure of the bare fiber to 589 K (600° F) in a forced-air convection oven shows higher weight loss of the high-strength fiber than of the high-modulus fiber. The bargraph in figure 9 shows weight loss of various lots of the high-strength fiber and high-modulus fiber. Although large variations were noted between fiber lots, the weight loss of the high-strength fiber is generally larger. A discussion of the effect of fiber chemistry and morphology on the elevated temperature behavior of graphite fibers is beyond the scope of this investigation; however, the results show that less graphitic, high-strength fibers oxidize at a higher rate.

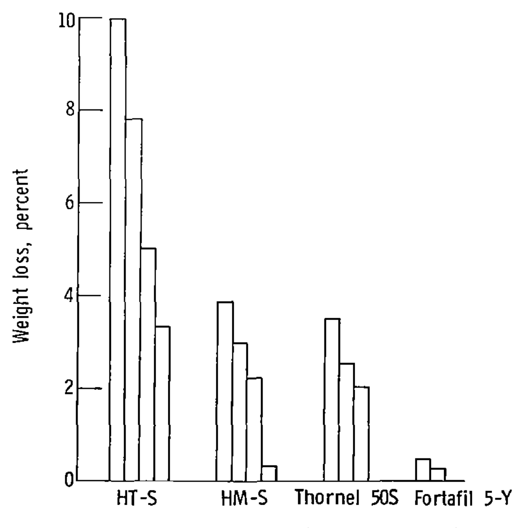

Figure 9. - Isothermal weight loss of graphite fiber exposed 1000 hours at (600° F). (Bars represent material from different lots.)

Long-Term Ambient Degradation

With graphite/epoxy systems it has been observed that long-term exposure to ambient temperature and humidity conditions results in loss of elevated temperature flexural strength. In figure 10 a comparison is made of the flexural strength of a HM-S graphite epoxy (Hercules 3002M) composite and graphite/P10P composites. The limited study reveals that the 449 K (350° F) flexural strength of the 3002M decreases significantly with time. No degradation is seen of the graphite/P10P composites flexural strength at 533 K (500° F) after 400 days exposure at ambient conditions.

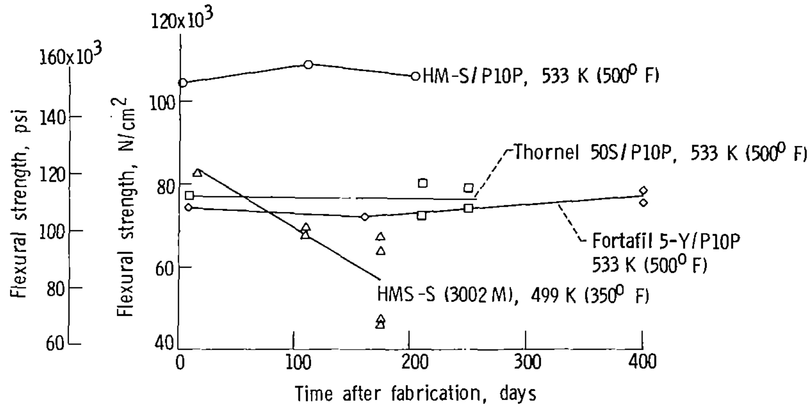

Figure 10. - Effect of long term ambient exposure on the elevated temperature flexural strength of graphite/P10P and graphite/epoxy composites.

SUMMARY OF RESULTS

The following results were obtained from an investigation of graphite/resin composites exposed and tested in air at 297, 533, and 589 K (75°, 500°, and 600° F):

1. Graphite/P10P composites fabricated in a matched-die mold had void contents less than three percent.

2. The 533 K (500° F) flexural strength, flexural modulus, and interlaminar shear properties were generally retained up to 1000 hours of exposure. At 589 K (600° F), however, the properties degraded significantly after 300 to 400 hours of exposure.

3. The percent reduction of elevated temperature properties compared with room temperature properties was greater for HT-S composites than for the HM-S, Thornel 50S, and Fortafil 5-Y composites.

4. Higher weight loss was observed for HT-S fiber than for the HM-S, Thornel 50S, and Fortafil 5-Y fibers after exposure at 589 K (600° F) in air for 1000 hours.

5. Properties of composites with high void content (8.9 percent) degraded at a greater rate at 533 K (500° F) than did low void composites at either 533 or 589 K (500° or 600° F).

6. No significant change of elevated temperature flexural strength was observed for graphite/P10P composites under long-term exposure (up to 400 days) at ambient temperature.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 29, 1971,
134-03.

REFERENCES

1. Burns, E. A.; Lubowitz, H. R.; and Jones, J. F.: Investigation of Resin Systems for Improved Ablative Materials. Rep. TRW-05937-6019-R0-00, TRW Systems Group (NASA CR-72460), Oct. 1, 1968.
2. Burns, E. A.; Jones, R. J.; Vaughan, R. W.; and Kendrick, W. P.: Thermally Stable Laminating Resins. Rep. TRW-11926-6013-R0-00, TRW Systems Group (NASA CR-72633), Jan. 17, 1970.
3. Hoggatt, J. T.; and Bell, J. E.: Development of Processing Techniques for Carbon Composites in Missile Interstage Applications. Rep. D2-125559-8, Boeing Co. (AFML-TR-69-98, AD-854522L), May 1969.
4. Browning, C. E.; and Marshall, J. A.: Graphite Fiber Reinforced Polyimide Composites. J. Composite Materials, vol. 4, July 1970, pp. 390-403.
5. Chamis, Christos C.: Mechanics of Load Transfer at the Fiber/Matrix Interface. NASA TN D-6588, 1971.
6. Pike, R. A.; and DeCrescente, M. A.: Elevated Temperature Characteristics of Boron and Graphite Fiber/Polyimide Resin Composites. Proceedings of the Society of the Plastics Industry 26th Annual Technical Conference, 1971, pp. 13-D1 to 13-D8.